The Safe Handling of Fluorine

Introduction

This supplement to the *Health &Safety Manual* describes the common hazards associated with fluorine and details engineering and procedural controls required for its safe use. This supplement is organized according to the process you must go through to safely handle fluorine at LLNL: (1) educate yourself on the chemical and physical hazards of fluorine, (2) design the fluorine system with appropriate engineering controls, (3) understand the procedure for purchasing fluorine, and understand the administrative controls for the safe use of fluorine and the maintenance of fluorine systems.

Because fluorine is a controlled item, you, the requestor, must contact your area Safety Team when operations require its use or the use of its inert gas mixtures. You will be directed to write an Operational Safety Procedure (OSP) and obtain an Engineering Safety Note for each operation. Your Safety Team will review the safety controls outlined in these documents and approve the purchase of fluorine if controls are judged to be adequate.

Treat mixtures of fluorine and inert gases with the same care as pure fluorine unless otherwise noted in this supplement or unless individual exceptions have been approved by your Safety Team. Document any exceptions in the operation's OSP and in an Engineering Safety Note.

Although fluorine is extremely hazardous, it can be handled safely if the proper precautions are taken. Only trained and competent personnel are permitted to handle fluorine; therefore, you should be familiar with the contents of this supplement and with such information as the Material Safety Data Sheet available from the supplier and the OSP and Engineering Safety Note associated with your operation.

This supplement covers pure fluorine, mixtures of fluorine in other gases and oxidizing fluorides such as XeF_6, ClF, ClF_3, ClF_5, and other halogen fluorides unless otherwise specified. Other reactive fluorides which are *not* vigorous oxidizers (i.e., HF, BF_3, WF_6, and NF_3) are not covered by this supplement.

Hazards of Fluorine

Chemical Hazards

Fluorine is a highly toxic and corrosive pale yellow gas whose sharp, penetrating odor is similar to that of a high concentration of ozone. The most powerful oxidizing element known, fluorine (a halogen) reacts readily with practically all organic and inorganic substances except inert gases, metal fluorides in their highest valence state, and a few pure and completely fluorinated organic compounds. However, even these few pure and fluorinated organic compounds may burn in a fluorine atmosphere if they are contaminated with a combustible material or are subjected to high flow rates of fluorine. (The chemical properties of fluorine are given in Table 1.)

Table 1. Chemical properties of fluorine.

Chemical symbol:	**F_2**
Molecular weight:	**38**
Cylinder pressure at 21°C	**2.0-MPa gauge (300 psig)**
Specific volume at 21°C and 1 atm	**0.634 m^3/kg (10.2 ft^3/lb)**
Specific gravity at 0°C (32°F) and 1 atm	**1.696 (air = 1)**

Hydrogen and fluorine combine with extreme violence, forming hydrogen fluoride. Fluorine also reacts explosively with most organic compounds. Moreover, it reacts with other halogen gases to form such compounds as ClF, ClF_3, BrF_3, and IFS. Although oxygen does not ordinarily react with fluorine, two oxygen fluorides, OF_2 and O_2F_2, do react with it. The extreme reactivity of fluorine demands that you properly clean and passivate a fluorine system prior to using fluorine in that system. *An explosion and fire may result if proper procedures are not followed.*

Health Hazards

Inhalation of fluorine gas can cause nose and throat irritation, respiratory tract and lung injury, unconsciousness, and even death. If fluorine makes contact with your skin or eyes, burns may result. These burns are caused by heat produced when fluorine or hydrogen fluoride (the result of fluorine reacting with moisture in the air) reacts with the moisture on the skin. Moreover, fluoride ions can penetrate deeply to the bone, replacing the hydroxide ions in the bone to produce injury.

Pain from injuries associated with fluorine exposures is often delayed especially if the fluorine is dilute. Therefore, if you even suspect you may have been exposed, rinse your skin and eyes with large amounts of water; continue rinsing for 20 min. Get immediate medical treatment. Appendix A describes the proper emergency procedures to be followed in the event of exposure to fluorine.

Hygienic Standards. According to the U.S. Department of Labor Occupational Safety and Health Administration,[1] the allowable limit for an 8-h time-weighted average exposure to fluorine in a 40-h work week is 0.1 parts per million (ppm). Fluorine gas is so irritating that humans will not tolerate excessive exposures to it. In one incident, brief inhalation of a concentration of 25 ppm caused acute toxic effects in humans.[2] In a study on mice, the lethal concentration for 50% of the mice after 60 min of exposure was 150 ppm.[3] Direct skin exposure to pure fluorine can cause severe burns in 0.2 s, and an exposure for as long as 0.6 s can result in thermal flash burns comparable to those produced by an oxyacetylene flame.[4]

Precautions for the Safe Use of Fluorine

Engineering Controls

As stated in *Pressure Vessel and System Design*, Supplement 32.03 of the *Health & Safety Manual*, *you* must ensure that an Engineering Safety Note is attached to the OSP for all toxic or corrosive gas systems; this includes fluorine systems. Whenever a change is made to a system you must obtain a new or revised Engineering Safety Note documenting that change. Direct any questions regarding Engineering Safety Notes to the Pressure Safety Manager or your Safety Team.

You are responsible for establishing the following engineering controls to preclude the release of fluorine into the work area.

Isolation. Closed systems, constructed to prevent the escape of gas into work areas, must be used for all fluorine operations within a building.

Gas Storage Cabinets. All cylinders or containers in use or ready-to-use status need to be kept in ventilated gas storage cabinets. Cylinders must be moved with their caps on until they have been put into and secured in a gas storage cabinet. Gas storage cabinets are commercially available for cylinders in ready-to-use condition. These were developed for the semiconductor industry and can be used without modification for fluorine/inert gas mixtures containing <5% fluorine. (10% fluorine/inert gas mixtures can be used to passivate these systems.) Gas storage cabinets need the following features:

- 18 gauge or thicker steel walls (minimum required by UFC Article 80) for fluorine/inert-gas mixtures containing ≤10% fluorine.
- The smallest doors consistent with safe cylinder handling. The doors must be self-closing and need louvers so the cabinet will be under flowing suction ventilation at all times (see the next item for air flow specifications).
- Self closing and self latching windows to make all routine valve adjustments other than those needed to remove old cylinders and install new ones. Air flow needs to be sufficient to maintain an inflow of air at an average velocity of 200 feet per minute (fpm) and never less than 150 fpm anywhere in

the plane of the fully opened window. Test smoke released in the window plane must never flow outward.

- Toxic gas detectors installed inside the cabinet.
- Cylinders must be rigidly clamped so that opening the supply valve will not cause torque to be transmitted to the regulator manifold (we have found that this can cause a leak). Cabinets used for pure fluorine, inert gas mixtures containing >10% fluorine, other gas mixtures and oxidizing fluorides should have bare-finish stainless steel walls. Such cabinets also need:
- Barricades to protect the operator.
- Valve handles that protrude through the cabinet wall to minimize the times when an operator must open the cabinet door or window and reach inside. Air velocities through the holes must be 500 fpm or more.

Delivery Hardware. Delivery pipes and tubes must be of all-welded construction or be double walled. The outer tubing must be under suction ventilation and be continuously monitored for gas leakage in a double-walled system. Double-walled and all-welded lines are recommended and may become mandatory in the future. All non-welded joints and fittings must be in enclosures that are under suction ventilation and monitored for gas leakage. The materials in all-welded lines and the inner tubes of double-walled lines must be made of compatible materials.

Compatible Materials. Compatible materials must be used. These are summarized in Appendix B for fluorine and fluorine/inert gas mixtures. Contact the material vendor for guidance about compatible materials for the material, temperature and pressure you will use. Additional guidance is available from your Hazards Control Field Team.

At room temperature, fluorine reacts slowly with many metals; this often results in the formation of a metal fluoride film that retards fluorine's effect on brass, iron, aluminum, magnesium, and copper. Hence, these metals are quite satisfactory for handling fluorine at room temperature. However, at higher temperatures, you must consult the manufacturer regarding the adequacy of the material to be used. For example, nickel and Monel are more resistant to corrosion from fluorine at higher temperatures.

Passivation of Equipment. All equipment used in fluorine operations must be thoroughly cleaned, degreased, dried, and passivated. *Never use pure fluorine to passivate fluorine equipment or systems.* Several procedures can be used for passivation. See Appendix C for examples of cleaning and passivation procedures. The type of procedure will depend on the system to be installed. Contact your Safety Team or the Industrial Hygiene Group of the Hazards Control Department for information on procedures.

You must describe the passivation procedure in the OSP for your operation. A passivation procedure checklist unique to your operation is desirable.

All systems must be flow tested ("dry-run") with dry, inert gas before passivation of the assembled system begins if such testing is feasible.

Discharging Fluorine or Fluorine-Like Materials to the Atmosphere. NEPA/CEQA requirements mandate discharging fluorine, any fluorine mixture, or reactive fluoride to the atmosphere in a controlled manner. See Supplement 12.03 of the *LLNL Health & Safety Manual* for further details about how to plan atmospheric discharge controls. The area Industrial Hygienist will specify the controls needed. Possible controls include:

- Rock salt beds. Useful for concentrated streams. The fluorine displaces the chlorine so a chlorine remover is needed just downstream. Chlorine is less reactive and somewhat less toxic.
- Caustic scrubbing followed by precipitation for large gas streams.
- Tall stacks for emergency releases. *Tall stacks are used only for discharging unplanned releases or when other controls for planned releases are not practical!* Use the cylinder leak time specified by the vendor, if possible, or assume a cylinder filled with liquefied gas voids in 30 min and a cylinder containing gas only will void in 5 min when planning for emergency releases.
- Cylinder size limits. Cylinder size limits can be used to reduce the height of a stack needed for emergency releases.
- Activated carbon was used for removing fluorine gas. This technique is no longer acceptable because it has been found that the fluorine can react explosively with the carbon. Keep any used carbon beds on hand in secure locations away from heat and call Hazards Control for guidance about disposal of them.

Purging. Any equipment that has contained fluorine must be thoroughly purged with dry, inert gas (such as nitrogen) and evacuated at least once before opening or refilling it. Purging by a sequential evacuation and inert gas backfill is preferred; backfill locations need to be as close to the fluorine/fluoride source as possible. Automated purge controllers need to be used whenever possible for sequential evacuation/ backfill purging to reduce the risk of human error during this tedious but critical process.

Gas Monitoring. Gas monitoring is needed where people are or could be present. Contact your Hazards Control Field Team for guidance about available sensors, alarms, and alarm annunciation requirements.

Labels and Signs. Labels, as shown in Fig. 1, need to be conspicuously posted near entrances to areas where fluorine is stored or used. Equivalent signs are needed for oxidizing fluorides (contact your Hazards Control Field Team to get these signs). In addition to the signs, information concerning the quantity of fluorine in use in the area should be posted at the entrance, along with emergency procedures to be followed in case of an accident. "No smoking" signs should also be posted where fluorine is stored or used. Lines carrying fluorine must be labelled once every 20 ft, at wall penetrations, and in concealed spaces. (It's a good idea never to run fluorine lines through concealed spaces!)

Inactive Gas Storage. Containers that are not in use or ready to be used (i.e., cylinders with valves shut and caps on and thoroughly sealed containers of materials such as XeF_6 need to be stored in protected outdoor locations or dedicated-use buildings where they are protected from temperature extremes, contact with rain or condensed moisture, and direct sunlight. Indoor storage spaces need to be vented at a rate of 1 cfm/ft^2 or 10 air changes per hour, whichever is greater. These storage areas must be normally locked and unoccupied and entrances need to be posted with appropriate warning signs. Combustible/flammable materials and reducing agents can not be stored in the same area.

No part of the cylinders should be subjected to temperatures higher than 52°C (125°F); therefore, place them away from radiators and other heat sources that could cause an excessive rise in temperature. CAUTION: *Never allow flame to come in contact with any part of a compressed-gas cylinder. Fluorine cylinders are not equipped with pressure-relief devices.*

Additional Design Precautions. Below are additional design precautions that you must take when working with a fluorine system.

Pipes and Fittings. Weld the pipes and fittings of lines that are not to be dismantled. Socket-weld fittings are preferable to butt-weld fittings because they are easier to keep free of slag and foreign matter during joining. However, butt-weld fittings are acceptable if shielded arc techniques are used.

Where welding is impractical, use threaded joints or tube fittings, as long as these fittings are contained in an exhaust ventilation enclosure. Permatex #2, manufactured by Loctite, is recommended as a pipe dope; apply it only after the first few threads of the male fitting are engaged. Parker Aircraft, Swagelok or Cajon fittings (or equivalent) may be used where small connections in the system are broken frequently.

Pressure Regulators. Regulators must be used on a high-pressure fluorine source to facilitate the safe handling of pressure. Using a double-valving system alone to control pressure is not acceptable.

The Instrument Shop will not supply a fluorine regulator unless you present the appropriate Engineering Safety Note or authorization from the Pressure Safety Manager. Ensure that all regulators are inspected and pressure tested by the Instrument Shop and are labeled with the LLNL pressure-tested label shown on page 17 of *Pressure Vessel and System Design*, Supplement 32.03 of the *Health & Safety Manual.*

Pressure-Relief Protection. For low-pressure work (3 psi or less), blow-out traps, similar to laboratory test tubes, are recommended to warn of blocked lines or vessels when spring-loaded valves or rupture disks are not available. These traps are filled with chlorotrifluoroethylene (Kel-F) polymer oil. The head of oil should not exceed a nominal 6 in. The trap(s) should be placed in a ventilated enclosure that can exhaust any accidentally vented fluorine. If a blow-out trap is needed, contact the Matheson Company, East Rutherford, NJ.

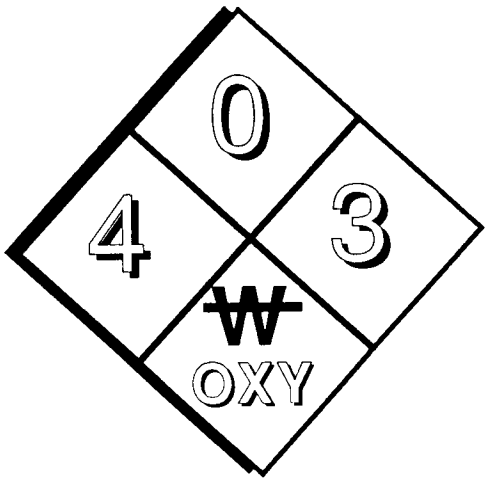
All components of fluorine systems using pressures above those protected by blow-out traps must have a rated working pressure above the maximum pressure that could accidently occur in the system. A safety factor of 5 to 8 shall be used in the system design.

DANGER

FLUORINE

Extremely hazardous gas! Causes serious chemical burns!

Will cause organic materials and flammables/combustibles to ignite!



Avoid inhalation. Avoid skin, eye, and clothing contact.

Has pungent, irritating odor.

For skin or eye contact, flood with water; get prompt medical attention.

Fig. 1. Standard warning for fluorine. It should be conspicuously posted by entrances to where fluorine stored or used and on the doors of gas storage cabinets. Available from Hazards Control.

When the maximum fluorine pressure could exceed the rated working pressure of any system component because of the pressure supply source or the heat involved in the operation, the system must be protected by a spring-loaded pressure-relief device or a rupture disk. When using a pressure-relief device, ensure that device is acceptable for use in a fluorine system. When using a rupture disk, the discharge from the disk must be directed into a local exhaust ventilation system or extended into an area where it can discharge safely. You must establish a regular program for replacing rupture disks to prevent corrosion from weakening the disks and causing them to fail prematurely.

Use of a three-disk system is recommended: the inner disk protects the center disk from corrosion by direct contact with gas. The center disk is rated to rupture at a designated pressure, and the outer disk protects the center disk from moisture corrosion.

Valves. All valves for fluorine service must have dissimilar metal-to-metal seating to prevent galling. They shall be provided with packless stem sealing and Monel or stainless-steel bodies. If packed valves are used, tetrafluoroethylene polymer shall be used in the stuffing box.

Gauges. Gauges with Monel or stainless- steel Bourdon tubes passivated for fluorine service shall be used. Gauges should be appropriate for indicating up to two times the pressures expected at the gauged points in the system.

Hydrogen-Fluoride Traps (Optional). Hydrogen-fluoride impurities can be removed from commercial fluorine using a trap containing sodium fluoride.

Flow Meters. Flow meters must be constructed of materials acceptable for use in a fluorine system.

Purge System. A purge system is required for experiments or operations using fluorine. The purge system must include an inert gas supply. This gas supply shall be protected from the fluorine system by use of fluorine-compatible check valves.

It may be desirable to treat the fluorine purged from the system rather than release it to the atmosphere. Your Safety Team will determine this need during the design phase of the system and will recommend procedures for treating fluorine exhaust.

Vacuum Pumps. Vacuum pumps campatible with fluorine systems must be used. To protect the pump, a soda-lime tower followed by a drier shall be included in the vacuum line to pick up trace amounts of fluorine. Vacuum pump systems using LN_2 traps shall have a relief device vented to a local exhaust ventilation system.

Eyewash and Safety Shower Facilities. You are responsible for ensuring that eyewash and safety shower facilities are located within 10 s travel time or 100 ft walking distance of your fluorine operation.

Administrative Controls

The *minimum quantity* needed to do a job must be used to minimize dangers to safety. Using minimum quantities of materials such as XeF_6 will also minimize the amount of material left over that must be disposed of as expensive hazardous waste. The *lowest fluorine* concentration that will do the job also needs to be used.

Two key administrative controls are OSPs and training.

OSPs. OSPs for fluorine operations need to specify:

- The quantity, concentration and type of material in storage and in use and where it will be stored and used.
- Personal protective equipment (including respirators).
- Passivation and cleaning procedures (also required in the Engineering Safety Note).
- Safety checklist.
- Procedures for dismantling and disposing of used equipment. Fluoride salts may be left over in lines and ducts being removed, but they are only modestly toxic and irritating so disposable lab coats and disposable respirators will often offer adequate protection from these salts (but not the gas). Exposures to massive amounts of fluoride residues will require whole body coveralls and more protective respirators. Fluorides are environmentally hazardous so fluorides and fluoride-contaminated items will need to be disposed of as hazardous waste. Residual fluorine, all fluorine mixtures, or reactive fluoride gases will need to be purged from systems and the fluorine/fluoride sources sealed (this means shutting the valves of cylinders and capping them). Contact your Hazards Control Field Team for guidance.

Training. Personnel need to take H5-503, “Pressure Safety Orientation,” H5-504, “Intermediate Pressure Safety,” and H5-512, “Fluorine Safety” before starting such work. Personnel also need to take the following before starting such work:

- H5-511, “Installers Practical Test” (for those who build or repair or assemble the system).
- H5-506, “Pressure Seminar for Engineers” (for those who prepare Engineering Safety Notes and design the system).
- Review the applicable OSP, Engineering Safety Note and this Supplement. Personnel preparing OSPs should also take H5-32, “Preparing an Operational Safety Procedure.” Fluorine users must also be aware of and follow these administrative controls:
- Personnel who transport or handle cylinders of pure fluorine, inert gas mixtures containing >10% fluorine, other fluorine mixtures and oxidizing fluorides need to be be warned that dropping, shocking or striking cylinders could cause an incident.
- Cylinders of fluorine, inert gas mixtures containing >10% fluorine, other fluorine mixtures, and oxidizing fluorides need to be transported in the back of an open truck.

— Personnel should never work alone when handling fluorine, including fluorine mixtures. Another person should always be within your sight and earshot, although not necessarily in the immediate area. (See "Working Alone," Sec. 26.15 of the *Health & Safety Manual.)*

— All components to be used in a fluorine system must be clean and free of organic material and bagged (or otherwise closed off to ensure system cleanliness until final assembly).

— All lines and equipment to contain fluorine should be pretested for leaks with dry nitrogen or helium.

— Repeated bending or excessive vibration of piping or equipment should be avoided. Either can cause the fluorine film that has developed in the system to flake and corrode valves and other system components. Excessive thermal cycling can also cause this problem.

Procedures and checklists must be agreed upon by your Safety Team, Industrial Hygienist, Pressure Safety Manager, and all other concerned parties before the system can be initially activated or reactivated after disassembly or modification.

- Systems containing fluorine under pressure must be inspected for leaks at frequent intervals. If you detect a leak, purge the system immediately and repair the leak. You can detect leaks using one of three methods:

1. Purge fluorine from the system and introduce helium.
2. Expel ammonia vapor at suspect leak points from a squeeze bottle containing ammonium hydroxide. A white mist will be observed if fluorine is leaking.
3. Use long metal tongs or forceps to place filter paper moistened with potassium iodide solution near suspected leaks. The paper will turn brown if fluorine is leaking.

- A regular program must be established for replacing rupture disks when such disks are used in the system.
- The possibility of valves freezing should be minimized by following these rules:

— Never use a regulator or manual control as the on-off control.

— When shutting down operations for any extended period, always close the cylinder valve and bleed the pressure in the regulator or manual control to atmospheric pressure.

— When the regulator or manual control is removed from the cylinder, replace the metal or plastic cylinder valve outlet cap originally provided.

— Use the proper wrench when opening or closing cylinder valves.

— Store cylinders in a dry, cool, well-ventilated area.

— While the cylinder is in use, rotate the valve stem at least once a day to break up any forming corrosion products.

— Use traps or check valves to prevent reverse flow.

— Obtain cylinders of a size that will ensure consumption in a short time. Suppliers usually carry a wide range of sizes to meet this need.

— Flush the regulator or manual control valve with dry nitrogen or dry air after use.

Returning Fluorine Cylinders. Before you return your cylinders to Industrial Gases, they must be inspected by an Industrial Hygienist or a Health and Safety Technician. Cylinders in good condition are returned by Industrial Gases to the gas supplier. Be sure to return the cylinders to Industrial Gases as

soon as possible, and do not overstock cylinders. Try not to keep these cylinders for more than one year from original delivery to you.

Affix a return tag for toxic/corrosive gases (see Fig. 2) to each cylinder before returning it to Industrial Gases. For additional questions on proper return procedures, refer to the Compressed Gas Cylinder Return and Disposal Procedure, which is available from your Safety Team, Industrial Gases, or the Pressure Safety Manager.

Disposing of Leaking or Damaged Fluorine Cylinders. When you find a leaking or damaged fluorine cylinder, notify the Fire Department immediately (ext. 2-7333). They will assess the situation, take action necessary to rescue or protect personnel, and ensure appropriate action is taken to contain the hazard. Hazards Control and Hazardous Waste Management will advise you on how to dispose of a leaking cylinder.

Dismantling Fluorine Systems. Consult your Safety Team prior to dismantling a fluorine system. The procedure for dismantling the system must be documented in the OSP for the experiment or a special OSP before dismantling can take place.

Procedural Controls

Experimenters need to:

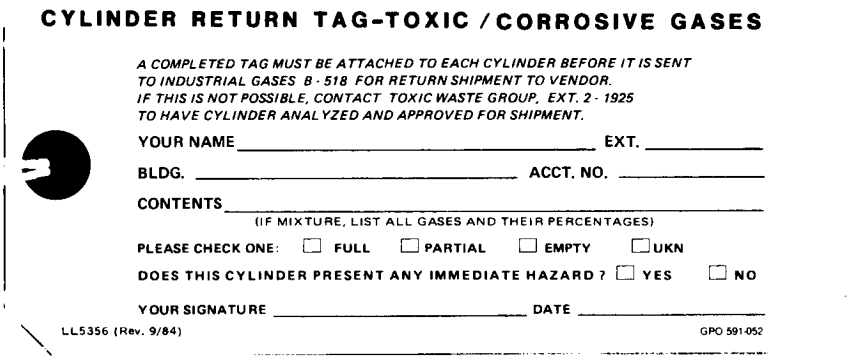
- Prepare an OSP per Chapter 2 of the LLNL *Health & Safety Manual* and an Engineering Safety Note per Supplement 32.03 of the LLNL *Health & Safety Manual.*
- Prepare a revised Engineering Safety Note and have it approved when a system handling fluorine, any fluorine mixture or oxidizing fluoride is changed.
- Arrange to have all unusual experiments involving fluorine peer reviewed in a manner similar to that used in planning HE experiments.

Requestors need to:

- Order elemental fluorine and all mixtures of it in cylinders with CGA 679 connections with valve closure torques not to exceed 50 ft-lb (state the closure torque limit in the procurement document).
- Have all orders signed by the Industrial Hygiene Group before the material can be delivered to the requestor. Direct deliveries to requestors are not permitted.
- Receive shipments personally and sign a receipt.
- Not allow incoming shipments to remain in hallways, unoccupied rooms and uncontrolled areas.

The Industrial Gas Section:

- Receives and logs in all incoming shipments at the gas dock, Building 518.
- Delivers it to the requestor and obtains a signed receipt of delivery.
- Stores it properly if it can not be delivered on the day it arrives at LLNL.
- Puts an expiration date tag on a cylinder along with an LLNL Delivery Tag. (Fig. 3).


CYLINDER RETURN TAG-TOXIC / CORROSIVE GASES

A COMPLETED TAG MUST BE ATTACHED TO EACH CYLINDER BEFORE IT IS SENT TO INDUSTRIAL GASES B-518 FOR RETURN SHIPMENT TO VENDOR. IF THIS IS NOT POSSIBLE, CONTACT TOXIC WASTE GROUP, EXT. 2-1925 TO HAVE CYLINDER ANALYZED AND APPROVED FOR SHIPMENT.

YOUR NAME _____ EXT. _____

BLDG. _____ ACCT. NO. _____

CONTENTS _____

(IF MIXTURE, LIST ALL GASES AND THEIR PERCENTAGES)

PLEASE CHECK ONE: ☐ FULL ☐ PARTIAL ☐ EMPTY ☐ UKN

DOES THIS CYLINDER PRESENT ANY IMMEDIATE HAZARD ? ☐ YES ☐ NO

YOUR SIGNATURE _____ DATE _____

LL5356 (Rev. 9/84) GPO 591-052

Fig. 2. Cylinder return tag for toxic/corrosive gases. This tag must be affixed to any fluorine cylinder to be returned to Industrial Gases.

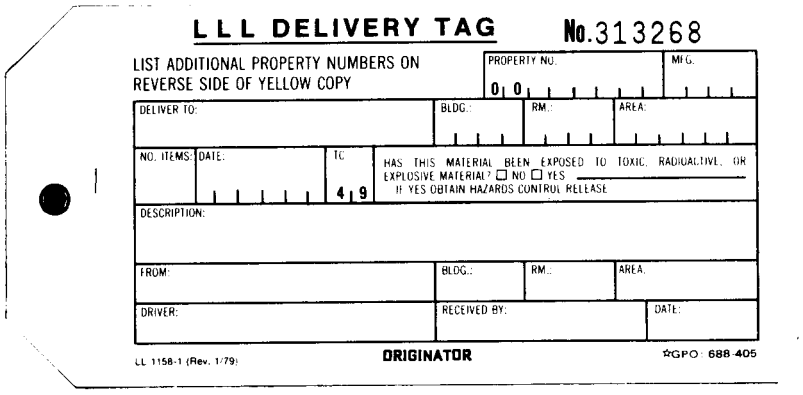


Fig. 3. LLNL delivery tag attached to each fluorine cylinder before Industrial Gases delivers that cylinder to its requestor.

Personal Protective Equipment

Protective equipment is routinely required; that is:

- Wear clean neoprene gloves when directly handling equipment that contains fluorine or has recently contained fluorine.
- Wear neoprene coats and boots to afford overall body protection for short intervals of contact with low-pressure fluorine. This clothing should be designed and worn so that it can be shed immediately.
- Wear safety glasses at all times. Metal frames are preferable to the customary plastic to eliminate the possibility of the frames catching fire. *Never wear contact lenses when working around fluorine.*
- Wear face shields made of chemically resistant polymers whenever you change cylinders or manipulate systems containing fluorine under pressure.
- You may also need to wear special respiratory protective equipment. Requirements for this special equipment will depend on the nature of the fluorine system installed and the special circumstances necessitating such equipment. Consult your Safety Team about these requirements.
- Personal protective equipment required for a fluorine operation must be detailed in the OSP. In addition, you must know the location of all personal protective equipment specified for your operation (including respiratory protective equipment) and the proper use and care of that equipment.

References

1. *General Industry OSHA Safety and Health Standards (26 CFR 1910),* U.S. Department of Labor Occupational Safety and Health Administration, Washington, D.C. OSHA 2206 (1983).
2. *Chemical Hazards of the Work Place* (J. P. Lippincott Co., Philadelphia, Pa., 1978), p. 271.
3. *Chemical Hazards of the Work Place* (J. P. Lippincott Co., Philadelphia, Pa., 1978), p. 271.
4. *The Matheson Company Gas Data Book,* 6th ed. (Matheson Gas Products, Inc., Secaucus, NJ., 1980) p. 331.

Appendix A

Fluorine Emergency Procedures

Calling for Help

In all accidents involving fluorine, notify the Fire Department using the emergency number for assistance: 2-7333 at Livermore; 3-5333 at Site 300.

Rescuing the Exposed Victim

Do not attempt to rescue a victim unless you are trained in emergency rescue, are adequately protected from any hazard, and have another trained and equipped person standing by. If you enter a heavily contaminated area, you must wear skin protection and use self-contained breathing apparatus or approved air-line equipment.

Treating the Exposed Victim

If That Victim is Someone Else

Skin and Eyes. Remove the victim from the contaminated area as soon as possible. Cleanse the fluorine from skin and eyes by flushing with copious amounts of water. Continue flushing for 20 min. As you flush, remove any contaminated clothing from the victim.

Inhalation. If you suspect a person has inhaled fluorine, move that person into the fresh air. If that person has stopped breathing, apply mouth-to-mouth resuscitation at once. Also treat the victim for eye and skin exposure by flushing the eyes and skin with large amounts of water. Do not delay emergency treatment; have someone else dial the emergency number.

Refer all affected persons to the Health Services Department, even when the immediate injury seems slight, and give the physician a detailed account of the accident.

If That Victim is You

Skin and Eyes. If your eyes are exposed to fluorine, do not rub them. Flush them with water for at least 20 min, lifting the upper and lower eyelids frequently to ensure complete washing.

If fluorine comes in contact with any part of your body or with your clothing, get into a safety shower immediately and flush your body with large amounts of water for 20 min. Wash thoroughly under your nails. Strip off any contaminated clothing as you wash.

Inhalation. If you have inhaled fluorine, leave the area immediately. Treat yourself for eye and skin exposure by flushing with large amounts of water.

No matter how slight the injury may seem, report it to the Health Services Department immediately, using the Fire Department for transportation. Emergency response personnel will ensure your clothing is washed before returning it to you.

Evacuating the Contaminated Area

In the Event of Leaks

If fluorine cylinders or equipment leak, evacuate the area immediately and dial the emergency number for assistance. Ensure no other personnel enter the area until the Fire Department arrives.

In the Event of Fire

Evacuate the area immediately and call for emergency assistance. Do not attempt to extinguish a fluorine fire. Ensure no other personnel enter the area until emergency response personnel arrive.

Appendix B

Accepted Materials for Fluorine System Components

Table B-1 consists of information on materials acceptable for use in fluorine systems. It is adapted from a table presented in the *Handbook of Compressed Gases*, 2nd ed. (Compressed Gas Association, Inc., 1981). This table is not intended to list all materials acceptable and available for use in fluorine systems.

When selecting system components for an operation, consult the manufacturer to ensure that those components selected are acceptable for use under the intended temperatures and pressures. At high temperatures, nickel or Monel is the material of choice. Teflon is the preferred gasket material. Air Force Manual 161.30, Volume II has useful information about halogen halides.

Table B-1. Acceptable materials for fluorine systems.

System component	Gaseous operation, normal temp	Liquid operation, low temp
Lines and fittings	**Nickel** **Monel[a]** **Copper[b]** **Brass** **Stainless steel 304L** **Aluminum 2017, 2024, 5052, 6061** **Mild steel (low pressure)**	**Monel** **Stainless steel 304L** **Copper** **Aluminum 2017, 2024, 2050**
Storage tanks	**Stainless steel 304L** **Aluminum 6061** **Mild steel (low pressure)**	**Monel** **Stainless steel 304L** **Aluminum 6061**
Valve bodies	**Stainless steel 304** **Bronze** **Brass**	**Monel** **Stainless steel 304** **Bronze**
Valve seats	**Copper** **Aluminum 1100** **Stainless steel 303** **Brass** **Monel[a]**	**Copper** **Aluminum 1100** **Monel**
Valve plugs	**Stainless steel 304** **Monel[a]**	**Stainless steel 304** **Monel**
Valve packing	**Tetrafluoroethylene polymer**	**Tetrafluoroethylene polymer**
Valve bellows	**Stainless steel, 300 series** **Monel[a]** **Bronze**	**Stainless steel, 300 series** **Monel** **Bronze**
Gaskets	**Aluminum 1100** **Lead** **Copper** **Tin** **Tetrafluoroethylene polymer** **Red rubber (5 psig)** **Neoprene (5 psig)** **Kalrez[c]**	**Aluminum 1100** **Copper**

[a] Monel is the material of choice for ≥10% F_2 mixtures or dilute F_2 at elevated temperatures and pressures.

[b] Stainless steel and copper tubing with TFE Teflon, FEL, or KEL-F may be used with 5% F_2 mixtures at room temperature.

[c] Kalrez is the material of choice for 5% F_2 mixtures.

Appendix C

Fluorine System Cleaning and Passivation Procedures

System Cleaning

System cleanliness and passivation are critical to the successful handling of fluorine. All equipment, lines, and fittings intended for fluorine service must be leak-tight, dry, and thoroughly cleansed of all foreign matter before use. The following procedure should serve as a *minimal* guideline to system cleaning. Experimental requirements may dictate a more thorough procedure, particularly for use with pure fluorine and reactive fluorides.

1. Wash and rinse thoroughly with hot water. Do not allow to dry.
2. Rinse with acetone.
3. Degrease with Freon TFE (Fr-113); vapor degrease where possible.
4. For polymers (Teflon or Kalrez), squirt Freon TFE onto a clean, lint-free wipe and then wipe the polymer clean.
5. Dry with clean, oil-free, dry air or nitrogen, or in a vacuum oven.
6. Assemble system and check for leaks at working pressure with an inert gas. A vacuum check is also desirable.
7. Evacuate the system to 4–5 μm or less, and at the same time heat to at least 120°C, or 10–20°C above operating temperature. Hold for 1 hr after base pressure is obtained.

Documentation that the system has been cleaned to at least these guidelines shall be maintained by the responsible individual / designer.

Passivation

The corrosion resistance of all materials used with fluorine depends upon the passivation of the system. This operation is intended to remove the last traces of foreign matter from the system and to form a passive fluoride film on the metal surface. At room temperatures, fluorine reacts vigorously with most metals to form this protective fluoride film; however, further reaction may be obtained by raising the temperature. For this reason, passivation must be accomplished at the working temperature and pressure of the system or a few degrees higher. Using the standard regulator manifold as an example, the following can serve as a guideline to system passivation. This procedure may be used for passivation with dilute fluorine mixtures:

CAUTION! Dropping, striking, or shocking the fluorine cylinders may result in an exposure incident.

1. Wear protective gear: safety goggles, full-face shield, flame-retardant gloves, and apron. A second person should be present.
2. Insure the vent blower system is operating. Insure the active fluorine detector is operating, if applicable.
3. Make a careful visual inspection of the exterior of the cylinder, valve, and CGA connection. Check for corrosion or mechanical problems. Verify the cylinder pressure tag at 500 psi or less.
4. Check the tightness of the packing nut—should be 40 ft-lb, nominally right-hand thread.
5. Slowly loosen the outlet cap. **CAUTION!** A cross scat leak may have pressurized the outlet.
6. Check the valve outlet and system inlet for foreign material (solid or liquid). **CAUTION!** Two connections are in general use in the fluorine industry: CGA670 and CGA679. Make certain that you have a match between the standard regulator manifold and the supply valve outlet.
7. Install a new gasket (degreased, dried, and lint free).
8. Insure that the air-operated valve is closed and the regulator on the manifold is backed out.
9. Attach the cylinder to the regulator manifold.

10. Clamp the cylinder to prevent torque from being applied to the regulator manifold upon opening the valve.

11. Attach a remote cylinder valve handle and close the barricade.

Remote temperature and pressure monitoring capabilities are desirable during the passivation process because pressure surges and rapid temperature rises are indicative of possible system failure.

1. Check the supply cylinder and upstream connections to the regulator for leaks at 500 psig with an inert gas source. Check the downstream connections for leaks at the working pressure.

2. Vent and evacuate the leak-check gas.

3. Close all valves and back off the regulator.

4. Open the fluorine-supply cylinder valve as gently as possible and close it immediately. Monitor the temperature in the exposed region.

5. After 10 min or when the temperature is ambient, open the air-operated valve. Note the pressure, and monitor the temperature in the newly exposed region.

6. After 10 min or when the temperature is ambient, set the regulator to 5 psig. Note the pressure drop on the supply gage, and monitor the temperature in the newly exposed regions. Back off the regulator, and monitor the 100-psi gage.

7. After 5 min or when the temperature and pressure are stable, set the regulator to 5 psig. The user may start passivating the system by opening the system valve on the regulator manifold. The user must follow the guidelines of slowly exposing sections of the system to increasing concentrations of fluorine until working conditions are achieved.

8. When the supply gage indicates approximately 50 psig, back off the regulator. Open the vent valve and vent the system to atmospheric pressure. Close the vent valve.

9. Gently open and immediately close the fluorine-supply valve. The supply gage should read the approximate cylinder pressure. Monitor the temperature and pressure as before.

10. After 5 min or when the temperature and pressure are stable, set the regulator to 10 psig.

11. After 5 min or when the temperature and pressure arc stable, set the regulator to 15 psig. Monitor the temperature and pressure.

12. After 5 min or when the temperature and pressure are stable, set the regulator to 20 psig. Monitor the temperature and pressure.

13. Back off the regulator. Vent the downstream system to atmospheric pressure. Close the vent valve.

14. Gently open the fluorine-supply valve. The supply gage should read the cylinder pressure.

15. Set the regulator to 10 psig. Wait 5 min or until the temperature and pressure are stable.
Set the regulator to 20 psig. Wait 5 min or until the temperature and pressure are stable.
Set the regulator to 30 psig. Wait 5 min or until the temperature and pressure are stable.

16. The manifold is now passivated for 30 psig maximum operating pressure and room temperature conditions.

17. If higher operating temperatures are to be used, repeat steps 8 through 16 at 25–50°C intervals.

CAUTION! Avoid vibration and bending of passivated surfaces. This may cause flaking or spalling of the fluoride film, exposing unpassivated surfaces and fouling valve seats. Avoid exposing system to air, or any gas containing water or organic materials.

Systems may also be passivated with pure fluorine by a slow and gradual exposure to increasing concentrations. Much smaller pressure increases must be used in conjunction with greater pressure measurement resolution. For example:

Vacuum of 1 μm or less	Hold for 15 min.
1 μm to 0.1 atm	Hold for 15 min or until the temperature and pressure stabilize.
0.1–0.3 atm	Hold for 15 min or until the temperature and pressure stabilize.
0.3–0.6 atm	Hold for 15 min or until the temperature and pressure stabilize.
0.6–1.0 atm	Hold for 30 min or until the temperature and pressure stabilize.
1.0–5.0 atm	Hold for 30 min or until the temperature and pressure stabilize.

All increases must be added slowly. The supply source must be valved out of the system between additions (to minimize the available fluorine if the reaction goes out of control). If operating temperatures are to be above room temperatures, repeat the above procedure at 25–50°C intervals to 10–20°C above the operating temperature.